Scattering Vector Dependence of Mutual Diffusion Coefficients for Rodlike Micelles in Aqueous Sodium Halide Solutions

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The dynamic light scattering for aqueous sodium halide solutions of hexaethylene alkyl ethers (CnEt, n = 10, 12, 14, 16) and tetradecyltrimethylammonium chloride and bromide (C14DAC, C14DAB) has been measured at various scattering angles. The scattering vector dependence of mutual diffusion coefficients can be classified into several types, relating with regimes of micelle concentration, that is, dilute, semidilute, and concentrated regimes. The curves with positive initial slopes are contributed to by the rotational diffusion besides the translational diffusion. On the other hand, curves with negative initial slopes are mainly originated by the translational diffusion and its anisotropy.

Introduction

Recently, many workers have been investigating the dynamic light scattering of aqueous micellar solutions. Nevertheless, there are very few reports associating with the scattering vector dependence of mutual diffusion coefficients for aqueous micellar solutions. Flambert and Pecora1 have measured the dynamic light scattering for 4 M NaCl solutions of dodecyltrimethylammonium chloride. The measurements were carried out at four scattering angles, and results were analyzed on the basis of the scattering theory for very large molecules.

Wilcox and Kaler2 have reported the dynamic light scattering measurement for aqueous solution of hexaethylene dodecyl ether with the surfactant concentration of 1.3 × 10–2 g cm–3 at several temperatures. They revealed that mutual diffusion coefficients increased with an upward convex curvature, as the square of the magnitude of scattering vector, μ = [(2πn0/λ) sin (θ/2)]2, increased, where n0 is the refractive index of solvent, λ is the wavelength of incident light, and θ is the scattering angle.

The dynamic light scattering for large molecules was theoretically formulated by a few workers. Pecora and co-workers8–10 derived equations of the field correlation function for flexibly coiled, rigid rod, and wormlike polymer chains in dilute solutions and rigid rod polymers in semidilute solutions. Fujime and Maeda8–9 have described theoretically the field correlation function from dilute, semidilute, and concentrated solutions of very long semiflexible filaments. Theories were applied to solutions of poly(γ-benzyl L-glutamate)11,12 and suspensions of fd virus.9

In the present paper, the dynamic light scattering is measured at various scattering angles for aqueous sodium halide solutions of nonionic and cationic surfactants in dilute, semidilute, and concentrated regimes. The dependence on scattering vector of mutual diffusion coefficients is classified into different types and is related with micelle concentration.

It has been confirmed that rodlike micelles are formed in aqueous sodium halide solutions of CnEt, C14DAC, and C14DAB examined here.11–14 Long rodlike micelles exhibited a semiflexible character in dilute solutions and were overlapped and entangled one another in semidilute solutions. Micelles in the concentrated regime behaved differently from those in the semidilute regime. Therefore, the scattering vector dependent dynamic light scattering for aqueous solutions of rodlike micelles in this work is discussed on the basis of the theory for semiflexible polymer chains in dilute, semidilute, and concentrated regimes.

Experimental Section

CnEt, C14DAC, and C14DAB were the same samples as previously used.11–16 NaCl and NaBr were heated for 1 h. Water was redistilled from alkaline potassium permanganate.

The dynamic light scattering was measured at a 488-nm wavelength on an Otsuka Denko dynamic light scattering spectrophotometer DLS-700.13,16 The scattering angle was changed from 20 to 150°. The temperature of the cell housing was varied between 20 and 45 °C. Solutions were filtered five times through a Millipore membrane filter.

The second-order field correlation function was measured in the homodyne mode. The first-order normalized autocorrelation function was analyzed by the cumulant method and the mean characteristic time width, Γ, was obtained.

The effective or mutual diffusion coefficient, D, can be evaluated by a relation of D = Γ/μ2. The mutual diffusion coefficient is a function of scattering angle and micelle concentration, c – cο, that is

\[
D = D'(_L)D'(_R')(c–c_0)/(_R – _R_0) 
\]

where D' and D' are the terms associated with the diffusion coefficients and the intra- and interparticle interference effects, respectively. D is the partial specific volume of a micelle, and k is the frictional virial coefficient. M is the molecular weight of a micelle, K is the optical constant of the static light scattering, and R and R' are the reduced scattering intensities at the surfactant concentration, c, and the critical micelle concentration, cο, respectively.

Results

Figures 1 and 2 show the scattering vector dependence of mutual diffusion coefficients for 4 M NaCl solutions of C12Et, 3 M NaCl solutions of C14Et, and 1 M NaCl solutions of C14Et at 25 °C. For dilute solutions of micelles, mutual diffusion coefficients increase linearly with an increase in μ2. When micelle concentrations are increased, the initial straight line in a plot of mutual diffusion coefficients against μ2 deviates downward at high scattering vectors.

As micelle concentrations are increased further, the upward deviation at low scattering vectors also manifests. The deviation

at low scattering vectors becomes stronger with a further increase in micelle concentration and, at last, mutual diffusion coefficients decrease with an increase in \( \mu^2 \) over all scattering vectors examined.

The scattering vector dependence of mutual diffusion coefficients was also observed for 4 M NaCl solutions of C10E7, 3 and 3.5 M NaCl solutions of C12E7, 1 and 2 M NaCl solutions of C16E7, and 0 and 0.1 M NaCl solutions of C16E7. The variation of the dependence is more intensive at high NaCl concentrations and for surfactants with a longer alkyl chain.

The scattering vector dependence of mutual diffusion coefficients is more remarkable for 2.6 M NaCl solutions of C12DAC.
coefficients deviate upward at low scattering vectors. Therefore, a curve decreases initially and then increases through minimum. (d) The minimum and the succeeding increase at high scattering vectors disappear and mutual diffusion coefficients decrease monotonously over all scattering vectors. (e) The mutual diffusion coefficients decrease steeply at low scattering vectors and become constant at high scattering vectors. The typical patterns are illustrated in Figure 5.

NaCl and micelle concentrations where patterns a–e are revealed are represented in Figure 6 for aqueous NaCl solutions of C12E7 at 25 °C. The same kind of diagrams against temperatures and micelle concentrations are given in Figure 7 for 1 M NaCl solutions of C14E7, 2.6 M NaCl solutions of C14DAC, and 4.3 M NaBr solutions of C14DAC.

Figures 6 and 7 also illustrate threshold micelle concentrations for overlap and entanglement of rodlike micelles. The threshold values above which rodlike micelles overlap one another were calculated on the basis of a wormlike chain model, and threshold values above which rodlike micelles entangle were obtained from a viscometric measurement. The crossover concentrations between semidilute and concentrated regimes were observed on a light scattering analysis and are included in Figure 6.

Figure 7. Diagrams of patterns a–e for aqueous sodium halide solutions of C14E7, C14DAC, and C14DAB as a function of temperature vs micelle concentration. (a) C14E7 in 1 M NaCl; (b) C14DAC in 2.6 M NaCl; (c) C14DAB in 4.3 M NaBr. L-L, liquid–liquid phase separation; s, separation of solid. The phase diagram is given by a micelle concentration of weight percent. The other symbols have same meanings as those in Figure 6.

Aqueous sodium halide solutions of C14E7, C14DAC, and C14DAB display phase separation, that is, the liquid–liquid phase separation at high temperatures and the separation of solid at low temperatures. Figure 7 includes phase diagrams for aqueous sodium halide solutions of C14E7, C14DAC, and C14DAB.

When micelle concentrations which present each pattern on plots of mutual diffusion coefficients against \( \mu^2 \) are compared with dilute, semidilute, and concentrated regimes of rodlike micelles, it is ascertained from Figures 6 and 7 that patterns a and b are observed at the dilute regime and the semidilute but nonentangled regime. The patterns b-d are mainly obtained at the semidilute and entangled regime, and patterns d and e belong to the concentrated regime. The participation between patterns and regimes of micelle concentration is given in Figure 5.

The mutual diffusion coefficients consist of terms associated with the diffusion coefficients and the interference effects, as described by (1). The contribution from these terms depends on the size and shape of micelles and regimes of micelle concentration.

1. The mutual diffusion coefficients for small micelles are independent of scattering vector, as shown in pattern 0 of Figure 6. The values are related to the total translational diffusion coefficient, \( D_0 \), as follows:

\[
D = D_0[1 + k_D(c - c_0)]
\]  

where \( k_D \) is the hydrodynamic virial coefficient.

Usually, spherical micelles are small; their aggregation numbers are around 50–100. For such small micelles, any scattering vector dependence of mutual diffusion coefficients was not observed and mutual diffusion coefficients obeyed (2).

2. For large micelles but at small \( R_0^2/\mu^2 \), mutual diffusion coefficients are described by

\[
D = D_0(1 + AR_0^2/\mu^2)[1 + k_D(c - c_0)]
\]  

where \( R_0 \) is the radius of gyration of a micelle and \( A \) is a constant. Therefore, mutual diffusion coefficients increase linearly with \( \mu^2 \), as seen in pattern a of Figure 5, and numerical values of \( R_0 \) and \( D_0[1 + k_D(c - c_0)] \) are given by the slope of a straight line.


Scattering Vector Dependence of Diffusion Coefficients

Scattering it is a technique used to measure the mobility of solute particles in a solution. The dynamic light scattering has been measured for rodlike micelles in aqueous sodium halide solutions and analyzed at small \( R_g^2 \) on the basis of (3). It is a general method for the determination of the diffusion coefficient of a micelle solution. For long semiflexible rodlike micelles and at large \( R_g^2 \), it is ensured that theoretical equations for the mutual diffusion coefficient are different at dilute, semidilute, and concentrated regimes, according to a transcription of a theory for long semiflexible polymer chains.

3. In dilute solutions of \((c - c_0) \leq (c - c_0)^* \), where \((c - c_0)^* \) is a threshold micelle concentration of overlap, the diffusion coefficient term of the mutual diffusion coefficient can be written by

\[
D'(\mu) = D_0 + (L_c^2/12)\theta f'(k) + (D_1 - D_{\perp})[f_2'(k) - 1/3]
\]

where \( L_c \) is the contour length of a rodlike micelle. \( \theta \) is the rotational diffusion coefficient. \( D_1, D_{\perp} \) are translational diffusion coefficients perpendicular and parallel to the rod axis, respectively, and have a relation of

\[
D_\perp = (D_1 + 2D_{\perp})/3
\]

and

\[
D'(\mu) = D'(\infty) = D_0 + (L_c^2/12)\theta - (D_1 - D_{\perp})/3
\]

If it is supposed that the contribution from the anisotropy of the translational diffusion is much smaller than those from the total translational diffusion and the rotational diffusion, the difference

\[
\Delta D'(\infty) = D'(\infty) - D'(\infty) = (L_c^2/12)\theta
\]

should be positive. Then the \( D'(\mu) \) value increases gradually with \( \mu \), and it is at a constant value at \( \mu \rightarrow \infty \), as seen in pattern b in Figure 5.

3.2. In the semidilute regime which is defined by \((c - c_0)^* \leq (c - c_0) \leq (c - c_0)^** \), where \((c - c_0)^** \) is a crossover concentration between semidilute and concentrated regimes, the diffusion coefficient term of the mutual diffusion coefficient can be described in the same equation as that for dilute solutions,9 that is

\[
D'(\mu) = D_{2s} + (L_c^2/12)\theta f_{2s} f'(k) + (D_{2s} - D_{2s,\perp})[f_2'(k) - 1/3]
\]

where the suffix \( 2s \) means that parameters with this suffix belong to semidilute solutions.

It is expected in the semidilute regime that the rotational diffusion and the perpendicular translational diffusion are restricted.9 Then

\[
\theta_{2s} = \theta_{2s}, D_{2s,\perp} = \theta_{2s} D_{2s,\perp}, \text{and } D_{2s,\perp} = D_1
\]

where \( \theta_{2s} \leq 1 \). Therefore

\[
D'(\mu) = D_{2s} + (L_c^2/12)\theta_{2s} - (D_1 - \theta_{2s} D_{2s,\perp})/3
\]

and

\[
\Delta D'(\infty) \approx (L_c^2/12)\theta_{2s} - (D_1 - \theta_{2s} D_{2s,\perp})/3
\]

As the micelle concentration is increased, the scattering vector dependence of the \( D'(\mu) \) value change complicatedly from pattern b to d through pattern c, owing to the compensation of contributions by the rotational diffusion and the anisotropy of the translational diffusion. Then numerical values of \( \beta \) and/or \( \beta' \) decrease from unity, and the difference, \( \Delta D'(\infty) \), changes from positive to negative, whereas the \( \Delta D'(\infty) \) value is zero at

\[
(D_1 - \beta D_{\perp})/3 = (L_c^2/12)\theta_{2s}
\]

3.3. For concentrated solutions of \((c - c_0)^** \leq (c - c_0) \), in the same way

\[
D'(\mu) = D_{c} + (L_c^2/12)\theta c f'(k) + (D_{c,\perp} - D_{c,\perp})[f_2'(k) - 1/3]
\]

and

\[
\theta_{c} = \theta_{c,\perp}, D_{c,\perp} = \beta' D_{\perp}, \text{and } \beta, \beta' \leq 1
\]

by using parameters with a suffix c, which represents "concentrated". In this region, the rotational diffusion and the perpendicular translational diffusion are depressed strictly, enough to satisfy a condition of

\[
(D_1 - \beta D_{\perp})/3 > (L_c^2/12)\theta_{c}
\]

Then at limits of \( \beta, \beta' \rightarrow 0 \)

\[
D'(\mu) = D_{c} = D_1/3
\]

and

\[
\Delta D'(\infty) \approx -D_{c}/3
\]

Therefore, as seen in patterns d and e in Figure 5, the \( D'(\mu) \) values decrease gradually with \( \mu \) and constrict to a constant value at \( \mu \rightarrow \infty \), since contributions by the total translational diffusion and its anisotropy are dominant. Concurrently the difference, \( \Delta D'(\infty) \), decreases with an increase in micelle concentration or with a more remarkable entanglement of rodlike micelles, until a value of \(-D_{c}/3 \) is reached.

Figure 8 plots the difference \( D'(\mu) - D'(0) = \Delta D'(0) \) as a function of micelle concentration for aqueous sodium halide solutions of \( \text{C}_6\text{E}_7, \text{C}_{14}\text{DAC}, \text{and } \text{C}_{14}\text{DAB} \). This parameter becomes a measure of how much contributions by the rotational diffusion and the anisotropy of the translational diffusion at \( \mu = 2\pi \Psi_0/\lambda, \) including the contributions from the interference effects. For all systems, the \( \Delta D'(0) \) values display positive and maximum around the micelle concentration where the apparent micelle aggregation number is largest in dilute solutions.13 At these micelle concentrations the rotational diffusion must mainly contribute, as discussed in 3.1.

The \( \Delta D'(0) \) values decrease gradually with increasing further the micelle concentration and become negative at high micelle concentrations. This change must indicate that the contribution by the rotational diffusion or the perpendicular translational diffusion decreases, as rodlike micelles entangle harder in semidilute and concentrated regimes, as described in 3.2 and 3.3.

The scattering vector dependence of mutual diffusion coefficients sometimes constrains to a constant value at large scattering vectors, as illustrated in pattern b or e of Figure 5. In such a case, the \( \Delta D'(0) \) value is equal to a difference

\[
\lim_{\mu \rightarrow -\infty} D - \lim_{\mu \rightarrow \infty} D = D'(0) = \Delta D'(0)
\]

Such values are marked by the filled symbols in Figure 8. Pattern b was observed for aqueous sodium halide solutions of \( \text{C}_6\text{DAC} \) and \( \text{C}_{14}\text{DAB} \) around micelle concentrations with the largest apparent micelle aggregation number in dilute solutions.13 The obtained \( D(0), D'(0), \) and \( \Delta D'(0) \) values are listed in Table I. The \( \Delta D'(0) \) values range from \( 0.22-0.65 \times 10^{-2} \text{ cm}^2 \text{s}^{-1} \). They are maximum at a micelle concentration with the largest apparent micelle aggregation number and are larger at lower temperature.
TABLE I: Characteristics of Semiflexible Rodlike Micelles in Dilute Regime

<table>
<thead>
<tr>
<th>T, °C</th>
<th>$T_c - c_p$, g cm$^{-3}$</th>
<th>$10^2D(0)$, cm$^2$ s$^{-1}$</th>
<th>$10^2D(0)(c)$, cm$^2$ s$^{-1}$</th>
<th>$10^2D(0)(c)$, cm$^2$ s$^{-1}$</th>
<th>$10^2\Delta D(\infty)$, cm$^2$ s$^{-1}$</th>
<th>$10^2\Delta L_c(\infty)$, cm</th>
<th>$10^2\Delta L_c(\infty)$, cm</th>
<th>$10^2\Delta(\sigma_1, 1/L_c, 1/L_c^{10})$</th>
<th>$10^2[-(D_1 - D_2)/3]$, cm$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_4$DAC in 2.6 M NaCl</td>
<td>20</td>
<td>0.483</td>
<td>0.17</td>
<td>0.50</td>
<td>0.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.095</td>
<td>0.26</td>
<td>0.64</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.203</td>
<td>0.11</td>
<td>0.59</td>
<td>0.48</td>
<td>3610</td>
<td>48.4</td>
<td>79</td>
<td>0.16</td>
<td>8.6</td>
</tr>
<tr>
<td>C$_4$DAB in 4.3 M NaBr</td>
<td>25</td>
<td>0.111</td>
<td>0.16</td>
<td>0.60</td>
<td>0.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.191</td>
<td>0.10</td>
<td>0.59</td>
<td>0.49</td>
<td>2500</td>
<td>66.1</td>
<td>79</td>
<td>0.13</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>0.332</td>
<td>0.09</td>
<td>0.42</td>
<td>0.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.036</td>
<td>0.23</td>
<td>0.45</td>
<td>0.22</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.191</td>
<td>0.10</td>
<td>0.64</td>
<td>0.55</td>
<td>3360</td>
<td>50.2</td>
<td>90</td>
<td>0.13</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>0.191</td>
<td>0.08</td>
<td>0.73</td>
<td>0.65</td>
<td>5500</td>
<td>42.6</td>
<td>42</td>
<td>0.11</td>
<td>11.0</td>
</tr>
</tbody>
</table>

*From ref 17.

TABLE II: Characteristics of Semiflexible Rodlike Micelles in Semidilute or Concentrated Regime

<table>
<thead>
<tr>
<th>T, °C</th>
<th>$T_c - c_p$, g cm$^{-3}$</th>
<th>$10^2D(0)$, cm$^2$ s$^{-1}$</th>
<th>$10^2D(0)(c)$, cm$^2$ s$^{-1}$</th>
<th>$10^2\Delta D(\infty)$, cm$^2$ s$^{-1}$</th>
<th>$10^2\Delta(\sigma_1, 1/L_c, 1/L_c^{10})$</th>
<th>$10^2[-(D_1 - D_2)/3]$, cm$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_4$DAC in 2.6 M NaCl</td>
<td>20</td>
<td>2.927</td>
<td>0.80</td>
<td>0.30</td>
<td>-0.50</td>
<td>-0.63</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5.946</td>
<td>1.23</td>
<td>0.16</td>
<td>-1.07</td>
<td>-0.87</td>
</tr>
<tr>
<td></td>
<td>4.029</td>
<td>0.96</td>
<td>0.20</td>
<td>-0.76</td>
<td>-0.79</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.029</td>
<td>1.21</td>
<td>0.21</td>
<td>-1.00</td>
<td>-0.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.029</td>
<td>0.60</td>
<td>0.29</td>
<td>-0.32</td>
<td>-0.53</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.927</td>
<td>0.94</td>
<td>0.30</td>
<td>-0.64</td>
<td>-0.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.029</td>
<td>1.05</td>
<td>0.34</td>
<td>-0.72</td>
<td>-0.68</td>
<td></td>
</tr>
<tr>
<td>C$_4$DAB in 4.3 M NaBr</td>
<td>25</td>
<td>2.001</td>
<td>0.39</td>
<td>0.09</td>
<td>-0.31</td>
<td>-0.78</td>
</tr>
<tr>
<td></td>
<td>3.011</td>
<td>0.50</td>
<td>0.05</td>
<td>-0.45</td>
<td>-0.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.001</td>
<td>0.47</td>
<td>0.09</td>
<td>-0.29</td>
<td>-0.82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.001</td>
<td>0.58</td>
<td>0.08</td>
<td>-0.51</td>
<td>-0.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.001</td>
<td>0.30</td>
<td>0.10</td>
<td>-0.20</td>
<td>-0.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.001</td>
<td>0.42</td>
<td>0.09</td>
<td>-0.33</td>
<td>-0.79</td>
<td></td>
</tr>
</tbody>
</table>

The $\Delta D(\infty)$ values for dilute solutions of semiflexible rodlike micelles correspond to

$$\Delta D(\infty) = \frac{\Delta D(\infty)}{D(0)} - \frac{D(\infty)}{D(0)} = \left(\frac{L_c}{L_c^2/12}\right)^{1/2}$$ (22)

according to (1) and (8). If numerical values observed and evaluated previously $^1, ^{17}$ are used for the evaluation of the $D(\infty)$ values, the rotational diffusion coefficient can be calculated, as listed in Table I. In Table I, the numerical values of the contour length and the persistence length are also included. The evaluated rotational diffusion coefficients are 42-90 s$^{-1}$ for rodlike micelles with contour lengths of 2500-5580 nm.

The equation of the rotational diffusion coefficient for semiflexible polymer chains was derived by Hagerman and Zimm. $^{21}$ However, the equation is valid to polymer chains with $0.05 L_c/2a < 2.5$, while the $L_c/2a$ values for rodlike micelles of C$_4$DAC and C$_4$DAB examined here are too large. Actually, the numerical values of the rotational diffusion coefficient calculated by their equation are not reasonable for rodlike micelles of C$_4$DAC and C$_4$DAB.

Flamberg and Pecora $^1$ measured the dynamic light scattering for 4 M NaCl solution of dodecylmyldiammonium chloride at 25 °C and evaluated the translational diffusion coefficient of 0.32$ \times 10^{-7}$ cm$^2$ s$^{-1}$ and the rotational diffusion coefficient of 1300 s$^{-1}$ for rodlike micelles of $L_c = 460$ nm, $a = 82$ nm, and $a = 2.05$ nm, where $a$ is the radius of a cross section of a rod.

Zhou et al.$^{22}$ determined the rotational diffusion coefficient of long polymer chains formed by cobalt monooleate soap molecules, by using the transient electric birefringent technique. Soap polymer chains of $L_c = 237$ nm and $a = 108$ nm exhibited the rotational diffusion coefficient of 32 s$^{-1}$.

The equation of the field correlation function by Fujiime and Maeda $^{38}$ was applied to dilute solutions of poly(γ-benzyl l-glutamate). Kubota et al.$^{10}$ obtained the rotational diffusion coefficients of $\sim 3000$ and $\sim 1800$ s$^{-1}$ for polymers of $a = 156.5$ nm and $a = 1.1$ nm with $L_c$ of 205 and 255 nm, respectively.

Figure 8. The difference, $\Delta D(180)$, as a function of micelle concentration for aqueous sodium halide solutions of C$_4$Br, C$_4$DAC, and C$_4$DAB. (a) Aquous NaCl solutions of C$_4$Br at 25 °C. NaCl concentration (M): O, 3; A, 3.5; □, 4. (b) Aquous NaCl solutions of C$_4$DAC at 25 °C. NaCl concentration (M): O, 1; A, 2; □, 3. (c) Aquous NaCl solutions of C$_4$DAB at 25 °C. NaCl concentration (M): O, 0; A, 1; □, 2. (d) 2.6 M NaCl solutions of C$_4$DAC. Temperature (°C): C, 20, △, 30, □, 40. (e) 4.3 M NaBr solutions of C$_4$DAC. Temperature (°C): C, 25, △, 35, □, 45. The filled symbols represent the $\Delta D(\infty)$ values.
The rotational diffusion coefficients for rodlike micelles of 
C14DAC and C14DAB are smaller than those of dodecylid-
methylammonium chloride and poly(γ-benzyl-L-glutamate)
blocks, depending on the long contour length.

Schmidt and Stockmayer\textsuperscript{23} presented approximately an equation

\[
D_1 - D_\perp = \left(\frac{3}{4}\right)D_0 \left[1 - 0.5(L_c/2a)^{1/4}\right]
\]

(23)

for semiflexible polymer chains. If (23) is transcribed to semi-
flexible rodlike micelles, the contribution by the anisotropy of the
translational diffusion, which is omitted in (8), can be described by

\[
-(D_1 - D_\perp)/3 = -(1/4)D_0 \left[1 - 0.5(L_c/2a)^{1/4}\right]
\]

(24)

Numerical values can be calculated by using the contour length
and persistence length of rodlike micelles and mutual diffusion
coefficients for 2.6 M NaCl solutions of C14DAC and 4.3 M NaBr
solutions of C14DAB reached a constant value at high µ
t. Constant values are listed in Table II, where the \( D(0) \) and \( \Delta D(\infty) \) values are also included. The \( \Delta D(\infty) \) values are negative, and their

absolute values increase with an increase in micelle concentration,
independent of the temperature.

The \( \Delta D(\infty) \) values in the semidilute and concentrated regimes
change from (13) to (20), with increasing micelle concentration.
At the high limit of micelle concentration, where the rotational
diffusion and the perpendicular translational diffusion are re-
stricted

\[
\Delta D(\infty) / D(0) = D(\infty)'(c-c_m,\infty) / D(0)'(c-c_m,0) - 1 = -1
\]

(25)

from (1) and (19). The \( \Delta D(\infty) / D(0) \) values were calculated and
included in Table II. They approach \(-1\) as micelle concentrations
are increased.

It is stated that, in solutions of rodlike molecules at higher
concentrations, the field correlation functions at nonzero scattering
angles decay in a double-exponential fashion.\textsuperscript{24} It is due to the
coupling of the restricted rotational diffusion to the translational
diffusion, in which the perpendicular translational diffusion is
precluded. Such non-single-exponential curves of the field cor-
relation function at finite scattering angles were observed for
aqueous sodium halide solutions of surfactants at the semidilute
and concentrated regimes examined here. This observation must
confirm that rodlike micelles in such surfactant solutions behave
similar to the rodlike molecules at high concentrations.

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Effect of Structural and Chemical Factors on the Acidity and IR Spectroscopic
Characteristics of Bridging OH Groups in Zeolites

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The nonempirical method with an STO-3G basis set is used to study the effect of both the geometric (structural factor)
and chemical (chemical factor) characteristics of bridging OH groups in zeolites on their acidity and vibrational frequencies.
It is shown that the acid strength of the OH groups is especially affected by changes in the chemical factor, while the vibrational
frequencies are particularly influenced by the changes in the structural factor. These conclusions following from quantum
chemical calculations are supported by the results of the IR spectroscopic studies of the isotopic adsorption of ND\(_3\) for a
series of zeolites, as well as by the data of MAS NMR measurements.

Introduction

This study will be devoted to investigation of the reasons for
heterogeneity of the acidic and IR spectroscopic characteristics
of the bridging OH groups in zeolites. Beaumont and Barthomeuf
have found\textsuperscript{1,2} that the effective Brønsted acidity, \( \alpha \), of Al sites
in the framework of faujasites (X, Y, and dealuminated) (i)
increases with increasing Si/Al ratio, (ii) reaches a maximum,
\( \alpha = 1 \), for Si/Al = 6, and (iii) remains constant with further
increase in the Si/Al ratio. The stretching vibrational frequencies
of these centers were found to exhibit analogous behavior: (i) an
increase in the Si/Al ratio in these zeolites results in a shift of
the high-frequency band, \( \nu_{OH} = 3660 \text{ cm}^{-1} \), to lower frequencies,

\( \nu_{OH} = 3630 \text{ cm}^{-1} \), is attained for Si/Al = 6, and (iii) for an Si/Al ratio higher than 6, the
vibrational frequency remains constant. It is well-known\textsuperscript{3,4} that
in dealuminated faujasites with Si/Al = 6 no Al atoms are located
in the nearest possible positions to another Al atom. Therefore,
these results indicate that substitution of Si for Al in the T site
of the >Si—OH—(Si<)—O—(Si<)—O—T< and >Si—OH—(Al<)—O—(Si<)—O—(Si<)—O—T< fragments of the lattice does not in-

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